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by

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Cage-like Precursor Formation From Extensive Cyclization in Sol-Gel Inorganic Condensation Polymerization

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ABSTRACT

In the sol-gel synthesis of silica by the acid catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS), the fractal dimension, density and homogeneity of the gel depends strongly on the reaction conditions such as the pH and water concentration. However, ^{29}Si NMR results have shown that gelation occurs consistently at 80% conversion. The 80% gel conversion is very high compared to the 30% predicted by random branching theory. These results suggest that cyclization is strongly favorable, forming, typically, the most compact three-dimensional cage-like precursor of expected diameter around 10Å.

INTRODUCTION

For organic condensation polymerization, Flory's random branching theory (RBT) has been successful in predicting the gel conversion and molecular size distribution [1]. The inorganic condensation polymerization processes in sol-gel reactions, however, are highly nonideal. For example, RBT fails to predict a range of gel structure (from weakly branched polymeric networks to colloidal particles) which can be produced from the hydrolysis and condensation of metal alkoxides (TEOS and TMOS) under different pH and water concentration [2-5]. Results obtained by Himmel and coworkers [5] show that the fractal dimension of the gels decreases with decreasing starting water concentration and solution pH (for pH values less than 2). Consistent with other results [2,3], gels produced with low water concentration at low pH were found to be weakly branched.

A deficiency of RBT is its exclusion of cyclization which is common in the alkoxide (silicon and alkyl-modified silicon alkoxide) systems. Four-membered rings (and, in some cases, three-membered rings) are found by ^{29}Si NMR [6-10], Raman spectroscopy [11,12] and GC-MS [13] in sols and gels. Moreover, the detection of several unassigned ^{29}Si NMR peaks has led researchers [6,10] to speculate the presence of other types of ring and cage-like structures. Consistent with these results, studies on the kinetics of the trimeric chain precursor has found that

ring closure is much faster than chain extension [14]. This result suggests that cyclization is kinetically favored. Extensive cyclization can lead to the formation of compact three-dimensional cage-like precursors.

In this paper, we investigate how nonideality in polymerization can explain observed gel structures by examining conversions using ^{29}Si NMR.

EXPERIMENTS

Absolute ethanol (containing 1% by weight of paramagnetic relaxing agent chromium(III) acetylacetonate) was added to TEOS (both used as purchased from Minnesota Grain Products and Aldrich, respectively), followed by aqueous HCl solution of desired pH. The sample was capped and kept at room temperature. ^{29}Si NMR spectra were acquired on a Varian VXR500 or a GE 500 spectrometer at 99.3 MHz. For each spectrum, 32 or 128 scans were acquired with a delay time of 10 s. The background glass signal was subtracted.

RESULTS AND DISCUSSION

1. Failure of RBT

Random Branching Theory (RBT) assumes that the reactivity of any functional group is independent of its neighbors and the size of its host polymer, and that only intermolecular reactions are possible. Although the underlying assumptions are highly ideal, RBT works remarkably well for most organic step polymerizations to predict the average degree of polymerization and the molecular size distribution as a function of the extent of reaction and the functionality of the monomeric unit [1].

For sol-gel inorganic step polymerization, however, the experimental results deviate significantly from the values predicted by random branching theory even during the initial period of reaction. An explanation that has been presumed by several groups [10,15-17] takes the form of a negative first shell substitution effect (FSSE), which is most clearly seen in the following way.

According to RBT, at any extent of reaction, the mole fraction of various x-mers decreases monotonically with x, where x is the number of repeat units in the molecule. On a molar basis, the

monomer should always be the most abundant molecule. Since linkages are formed randomly, they should be randomly distributed among all the monomeric units, and, consequently, the molecular size distribution decreases monotonically with increasing size.

Unlike the prediction of RBT, results obtained from gas chromatography on an acid-catalyzed TEOS polymerization [18] show a non-monotonic decrease in the mole fraction of x-mer. This has also been noted independently by other workers [10]. Resistance to forming larger molecules causes monomers to be depleted more quickly than larger oligomers. The functional groups on a monomer are more reactive than the larger molecules. For low molecular weight species, this phenomenon can be explained by a negative first shell substitution effect, i.e. the hydroxyl group on a silicon becomes less reactive as the silicon is bonded to more siloxane bridges.

However, the negative FSSE approach does not address the tendency for ring formation. Moreover, as reactions progress, diffusion effects may become important due to decreasing host polymer mobility or inhomogeneity which arises from aggregation of cycles.

2. Conversion as pH and water concentration vary

So far, we have learned that the polymerization of TEOS deviates from the predictions of RBT and simple FSSE. We intend to learn how nonidealities vary with pH and water concentration, and if the trends display any consistency with observed change in gel structures. A convenient measure of the extent of polymerization is the conversion of functional groups.

TEOS polymerization occurs by the formation of siloxane bridges between two silicon atoms of valency 4, represented by the following equations:

$$\text{Si–OH} + \text{RO–Si} \rightarrow \text{Si–O–Si} + \text{ROH} \qquad (1)$$

where R can be H or CH_3CH_2. The conversion (α) of the polymerization process (regardless of which reaction or combination of them is responsible), defined as the fraction of the maximum possible number of siloxane bridges (e.g. for SiO_2), can be determined from the ^{29}Si NMR results to be:

$$\alpha = \frac{1}{4}\sum_{i=0}^{4} i\ [Q_i] \qquad (2)$$

where $[Q_i]$ is the fraction of the silicon site bonded to i siloxane bridges.

Early in reaction (Figure 1), conversion rate is dependent on pH and water concentration, suggesting different precursor formation. However, as shown in Figure 2, beyond a conversion of 60-70%, conversions all slow down and approach 80% towards gelation! The 80% gelation conversion is observed over a wide range of pH values and water concentration, consistent with data tabulated from the literature, as shown in Table 1. For the conversion measured in this group, series of spectra were obtained prior to gelation, showing insignificant changes in conversion as the liquid was approaching gel point. The conversion at gelation (α_g) is measured for a near-gelling sol, and is checked with ^{29}Si MAS.

Table 1: Universal conversion at gelation for TEOS polymerization

Water-to-Silicon	pH	α_g
4	1.0	0.84
4	1.3	0.83
4	1.5	0.83
4	2.0	0.83
6	2.1	0.82
10	2.5	0.83 [19]
10	4.3	0.83 [20]
16	1.9	0.84 [21]

The consistently high 0.83 conversion at gelation for these gels is astonishing. First of all, this value is much higher than that predicted by the Flory's random branching theory. According to the random polymerization theory which assumes that all functional groups are equally reactive and that intramolecular reactions are absent, the gelation conversion for a monomeric unit which is capable of forming 4 linkages should be 0.33 [1]. Of course, we would expect higher conversion since monomer is not in fact 4 functional over course of reaction, but rather increases in functionality with time.

Numerous ^{29}Si NMR results from the literature indicate that the rate of hydrolysis relative to condensation varies with water-to-silicon ratio and solution pH. Thus, as the reaction conditions change, we expect to observe initial polymerization of monomers of functionality

ranging from 4 (for systems with rapid hydrolysis followed by slow condensation) to 2 or 3 . With water-to-silicon ratio larger than the stoichiometric requirement of 2, we expect virtual complete hydrolysis of all monomeric units eventually. In other words, the monomer functionality in different systems is expected to increase at different rates, though eventually reaching the maximum value of 4. If all functional groups are equally accessible and cyclization is absent, as assumed even with FSSE, the conversion at gelation should vary. According to results from light scattering studies [2,3,5], the fractal dimension of polymers and gels should decrease with decreasing solution pH and water concentration. However, gelation occurs consistently at 80% conversion.

The observed universal high conversion suggests that irrespective of the initial functionality of the monomers, some functional groups are consistently not as effective towards the building of molecular weight. Some other factors are apparently at work to balance out the initial differences in "functionality". This can be due to cyclization and diffusion limitations. While high water concentration tends to promote hydrolysis, it is also expected to promote cyclization. Thus, it is possible that increased cyclization reduces the effective fucntionality of the monomeric units. The high 80% conversion suggests extensive cyclization, possibly occurring early in reaction which explains the initial rapid rise in conversion. Further reactions involve connection of these cycles which should require lower fraction of siloxane bonds, and can explain why conversion does not seem to depend on prior reaction conditions. Negative FSSE also tends to reduce the effective functionality by discouraging branching. Moreover, as the average molecular weight increases, the fraction of functional groups located inside a cluster (as opposed to being in the periphery) increases. If diffusion effects are important, that is the rate of encounter between any two groups becomes significantly low, these functional groups are relatively inactive with respect to polymer growth.

3. Cyclization

Three-membered and four-membered rings are found in abundance by ^{29}Si NMR [6-10] and Raman spectroscopy [11,12] early in reactions. Moreover, the detection of several unassigned ^{29}Si NMR peaks has led researchers [6,10] to speculate the presence of other structural units. A variety of ring and compact cage-like precursors has been identified by ^{29}Si NMR in aqueous potassium silicate solutions which make zeolites [22-24]. Thus, it is not at all impossible that these precursors are also present in the acidic systems. Can the presence of any of these precursors, formed from extensive cyclization, explain the high 80% conversion?

Extensive cyclization means that there is a strong spatial correlation between reactive groups. Existing polymerization models can, at best, give a crude estimate of the effect of intramolecular reactions. Nevertheless, gelation conversion can be estimated by treating different proposed ring or cage-like precursors as polyfunctional random branching "monomeric" units. For example, a cubic precursor, $Si_8O_{12}(OR)_8$ (OR is the functional group), is considered an eight-functional "monomeric" unit. In general, the conversion from f-functional "monomeric" units, T_0, is given by:

$$\alpha_{(T)} = \frac{1}{f}\sum_{i=0}^{f} i\ [T_i] \qquad (3)$$

where $[T_i]$ is the fraction of T-unit with i intermolecular bridges. The total fraction of siloxane bridges, which includes the intramolecular bonds within the cage, is:

$$\alpha = \frac{1}{2}\left\{ \frac{f\ \alpha_{(T)}}{2S} + \frac{C}{S} \right\} \qquad (4)$$

where S = number of Si-sites per T-unit

C = number of intramolecular bonds per T-unit.

Gelation conversion from random branching of the T-units is given by:

$$\alpha_{(T)} = \frac{1}{f-1} \qquad (5)$$

Thus,

$$\alpha = \frac{1}{2}\left\{ \frac{f}{2S\,(f-1)} + \frac{C}{S} \right\} \qquad (6)$$

Figure 3 shows the calculated gel conversion for different precursors that have been detected in aqueous potassium silicate solutions [22-24]. The observed high 80% conversion implies not only that cyclization occurs, but it occurs extensively early in reactions, leading to the formation of the most compact three-dimensional double three-membered ring precursor (D3R, using the symbol in zeolite science). A structure that can possibly be more compact than D3R is if four silicons are involved in a three-dimensional framework. However, experimentally observed O-Si-O bond angle ranges from 98° to 122°; while the more flexible Si-O-Si bond angle can range from 120° to

180° [25]. Even with the most strained O-Si-O and Si-O-Si bonds, the four-silicon three-dimensional framework is impossible to build. Note that the flexibility of the siloxane bond may explain why cyclization is so prevalent in silicate systems.

The Si-O bond length has been measured in silicate structures to be between 1.57 Å and 1.72 Å [25]. This gives the longest dimension in the D3R structure to be about 4.5 Å. Including the alkoxy or silanol groups, the longest dimension should be around 10 Å. This 10Å compact structure is consistent with the "particulate" building units proposed by Iler for the polymerization of silica in aqueous systems [26].

We propose that the D3R structure is only a typical precursor. It is expected that other precursors are also present in the solutions, and the formation of these precursors can be influenced by the initial reaction conditions.

CONCLUSIONS

In the acid catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS), gelation is observed by ^{29}Si NMR to occur at 80% conversion over a wide range of initial reaction conditions which should yield gels of various fractal dimension, density and homogeneity. The 80% conversion is much higher than the 30% predicted by random branching theory. These results suggest that cyclization occurs extensively early in reaction, forming, typically, the most compact cage-like precursor of expected diameter around 10Å.

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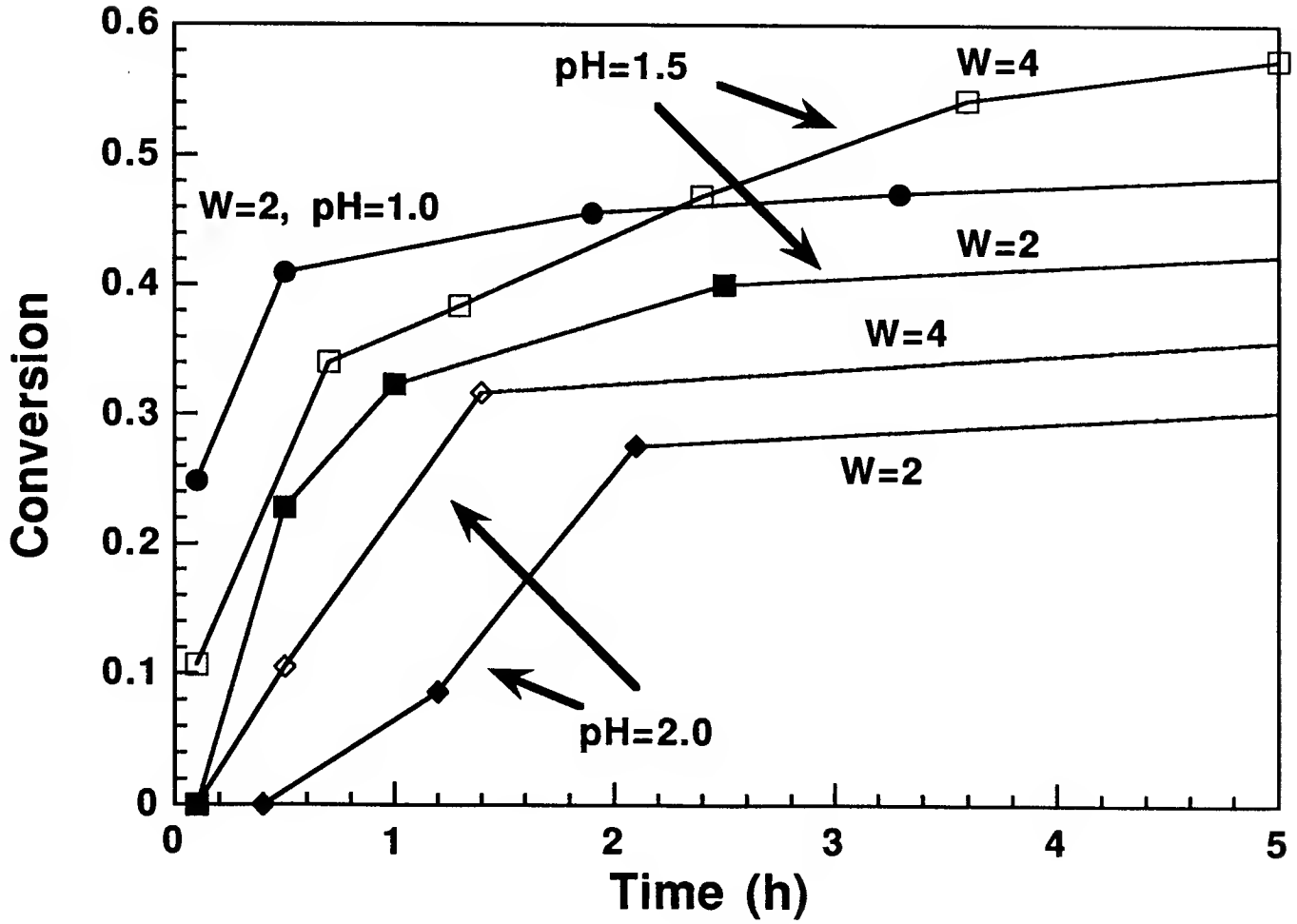
FIGURE CAPTIONS

1. Hydrolysis and Condensation of TEOS: Conversion at different pH and water concentration (early reaction).
   molar ratio TEOS : EtOH : H_2O = 1 : 4 : W

2. Hydrolysis and Condensation of TEOS: Conversion at different pH and water concentration (long time)
   molar ratio TEOS : EtOH : H_2O = 1 : 4 : W

3. Random branching of precursor: gelation conversion.

Figure 1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0.4
0.3
0.2
0.1
0
Conversion
0
1
2
3
4
5
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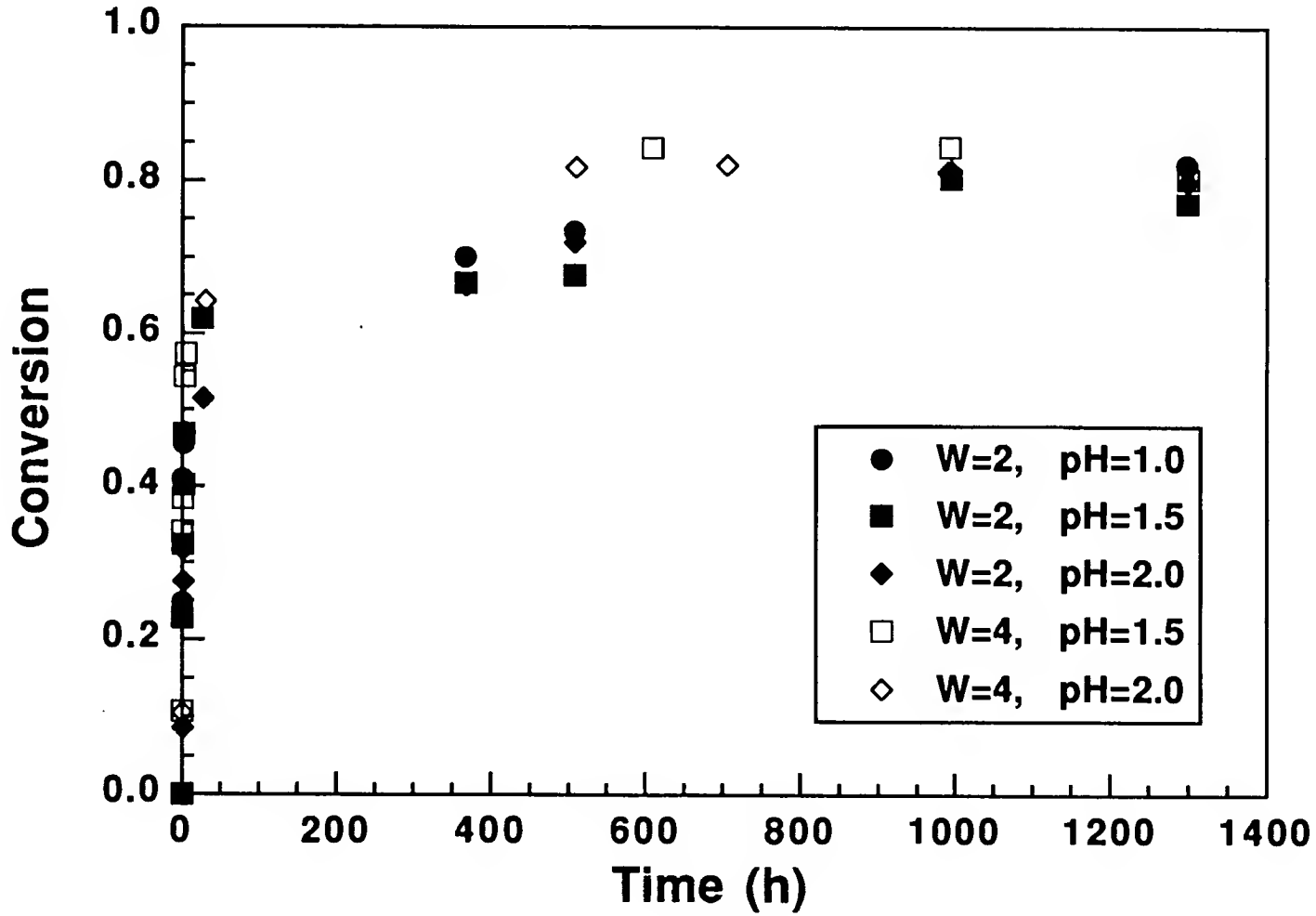
W=4
W=2, pH=1.0
W=2
W=4
W=2
pH=2.0

Figure 2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0.6
0.4
0.2
0.0
Conversion
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600
800
1000
1200
1400
Time (h)
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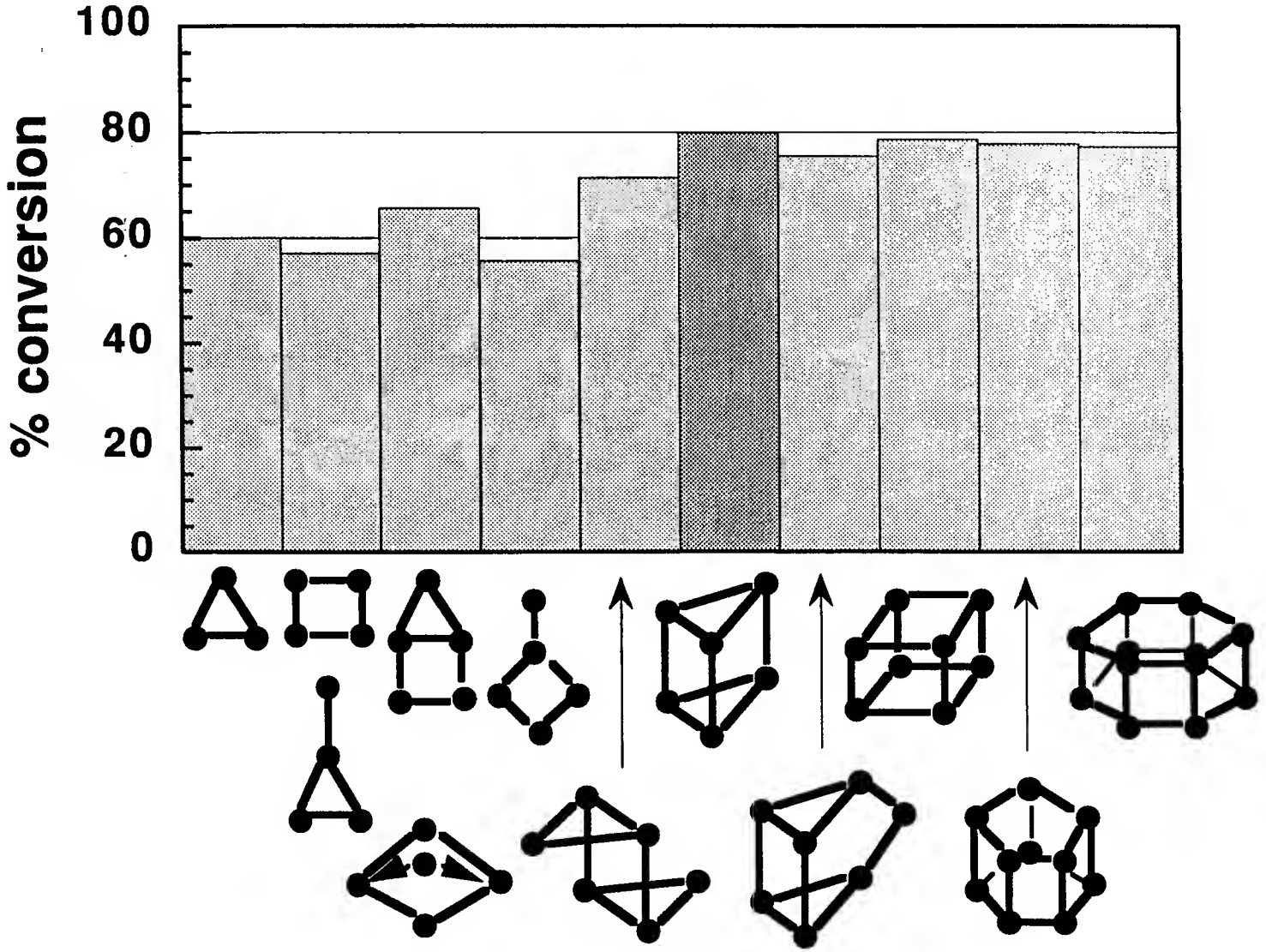
Figure 3